

## **DECONTAMINATION OF RADIOACTIVELY CONTAMINATED SCRAP METALS FROM DISCS**

[0001] This application claims the priority of U.S. Provisional Application Serial Number 60/230,153 filed September 1, 2000.

### **BACKGROUND OF THE INVENTION**

#### **Field of the Invention**

[0002] The present invention relates to systems and processes for decontaminating radioactively contaminated metal. In particular aspects, the invention relates to the removal of technetium and other actinides from nickel or other transition metals.

#### **Description of the Related Art**

[0003] The current effort to decommission weapons facilities requires processing of large amounts of radioactively contaminated scrap metal. The scrap metal includes, but is not limited to steel, copper, aluminum, and nickel. Opportunities exist to recycle these metals if the metals can be decontaminated to levels acceptable for release. There are, for example, approximately 8,500 tons of nickel in the form of cylindrical, contaminated ingots remaining from maintenance and upgrade of the Paducah and Oak Ridge Gaseous Diffusion Plants. The nickel is contaminated with technetium and uranium with possible contamination from other actinides. If the contaminants can be effectively removed from this nickel, the nickel may be recycled for other uses. The removal of technetium from the nickel is a particularly difficult part of the decontamination process since the nickel is contaminated throughout the volume of the metal (volumetrically contaminated) with technetium, and technetium is chemically similar to nickel in many respects.

[0004] Typically some form of electro-refining is used to separate technetium from the nickel. Many conventional electro-refining techniques purify nickel that is in a powdered form. U.S. Patent

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No. 5,217,585 issued to Snyder et al., for example, describes a decontamination process in which the nickel or other transition metal has been powdered and then dissolved in an aqueous acid solution prior to separation. Unfortunately, powdered nickel presents a handling problem, and it is costly to reduce large amounts of solid nickel to powder.

[0005] Other methods are known wherein the contaminated metal is present in a formed plate that is then used as an anode in an electrochemical process. Plate electrodes are a superior alternative to powders from a handling perspective, but the creation of plate electrodes using conventional methods is also costly and time-consuming. Typically, the anode plates used are flat, rectangular plates composed of nickel sulfide matte. If pure nickel were cast in this fashion, the mold/nickel interface cools first and the solidification is from that interface toward the free surface. This manner of cooling results in an anode that is structurally vulnerable to tensile forces and which may fail structurally during the dissolution process.

[0006] Also, the rectangular shape of the anode, when used with a rectangular cathode, results in uneven plating of the cathode. Ions released from a dissolving anode tend to spread angularly outward with respect to the center of the anode as they move toward the cathode. This angle is known as a throwing angle. As a result of this phenomenon, the edges of the cathode plate at a much greater rate than the center portions of the cathode. This uneven plating can present a problem when a cationic membrane is placed proximate to the cathode as the growing edges may impinge upon the membrane prematurely, perhaps causing the cathode to become contaminated.

[0007] U.S. Patent No. 5,262,019 issued to Snyder et al. describes processes for decontamination of radioactive metals wherein the irradiated nickel is prepared using “shot” production or thin sheet rolling from contaminated ingots. In the “shot” production process, the nickel is melted and cast into

fine particulates. Many of the same handling problems that exist with powders also are present with shot. Thin sheet rolling of ingots involves wrought processing wherein the ingot is heated and then rolled out into a thin sheet that is then cut up and used as an anode.

[0008] U.S. Patent No. 5,458,745 issued to Hradil describes methods of reducing technetium levels in nickel using electro-refining techniques wherein the radio-contaminated metal to be purified is used as the anode in an electro-refining cell. In practice, these electrodes are long rectangles of nickel, typically measuring about 4" in width and 3' long. The solution in which the anode and cathode are disposed is flowed through a pair of filters and a packed bed of powdered nickel. Hradil's method suffers from operational problems. The anolyte is treated and returned to the cell in the catholyte solution (which is commonly performed in industry). However, in this application, combining the anolyte and catholyte in this manner contaminates the catholyte and therefore the product nickel. Also, the packed nickel bed is quickly depleted of fresh nickel surface with which to provide a cementation reaction. This renders the system ineffective for technetium removal. Frequent changeout of this contaminated material creates a disposal issue.

[0009] It would be desirable to have devices and methods that address the problems of the prior art.

### **SUMMARY OF THE INVENTION**

[0010] A decontamination method and system is described wherein contaminated nickel anodes are obtained by cutting cylindrical nickel ingots into wafers having a disc shape. Each of the disc-shaped wafers is then used as the anode in an electro-refining process. The anode is dissolved in the process, thereby generating nickel ions and pertechnetate ions in solution. The process has numerous advantages as compared to previously used processes. First, the cost and time-consuming

steps relating to casting or molding nickel sulfide anodes are eliminated. Secondly, the plating process is improved through more uniform plating of the cathode. Third, the anode itself has improved mechanical strength.

[0011] An exemplary decontamination process is described wherein an electro-refining dissolution cell uses a technetium-contaminated nickel disc as an anode. A cationic membrane assembly separates the cathode from the anode, thereby providing an anode chamber and a cathode chamber within the cell. An anolyte solution, such as Watts nickel electrolyte, surrounds the anode in the anode chamber while a catholyte solution surrounds the cathode in the cathode chamber. The cationic membrane between the anode and cathode keeps the technetium from passing from the anolyte into the catholyte. In this manner, the catholyte, and therefore the cathode, remains contaminant free. Anolyte solution is pumped from the cell, treated using a separate electrolytic process, and returned to the anolyte. The anolyte and catholyte solution remain separated and are not mixed.

[0012] The anolyte treatment process (technetium trap) consists of an electrolytic process operated at a low amperage. In this process, small amounts of nickel are plated and the technetium, attracted to fresh nickel surface, plates out with the nickel. This allows capture and disposal of the technetium contamination. A filter is incorporated prior to the technetium trap to remove particulate matter from the electrolyte.

[0013] In operation, a portion of the nickel ions from the dissolving anode in the electrorefining cell pass through the cationic membrane and are plated out on the cathode. The pertechnetate ions (from the technetium in the anode metal) are unable to pass through the cationic membrane and are prevented from plating with the nickel on the cathode. Uranium and other actinides will not plate

onto the cathode. These contaminants are expected to remain in solution or deposit as slimes in the cell or anode bag.

[0014] The anode in the electro-refining cell is a disc-shaped wafer of substantially pure nickel that has typically been cut from a larger cylindrical ingot. Examples of such ingots are those found at the Paducah Gaseous Diffusion Plant. These ingots are approximately 25 inches long, 25 inches in diameter and weigh approximately 2000 lbs. To make a disc anode, the ingot is cut into a plurality of wafers.

[0015] There are advantages to use of the wafers. The wafers can be saw cut directly from existing ingots thereby decreasing the cost and time associated with melting and recasting the ingots. A further benefit is provided by the specific metallurgical nature of the wafers. The inherent cooling process of the cylindrical ingots and the round shape of the wafers lends mechanical strength to the anode and assists in providing more uniform plating of the cathode. Testing has shown the inventive process to be highly successful and, in fact, unexpectedly successful in decontaminating nickel.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0016] Figure 1 is an isometric-view schematic diagram illustrating an exemplary decontamination system incorporating an electro-refining cell in accordance with the present invention.

[0017] Figure 1A is a side, partial cross-sectional view schematic diagram of the system shown in Figure 1.

[0018] Figure 2 is a plan view of the anode and cathode used in the system illustrating a preferred positioning and spacing.

[0019] Figure 3 is an end-on view of the cathode used in the system shown in Figures 1 and 2.

[0020] Figure 4 is an end-on view of the anode used in the system shown in Figures 1 and 2.

[0021] Figure 5 illustrates an exemplary nickel ingot in side cross-section. illustrating the various formation zones associated with the ingot.

[0022] Figure 6 is a cut-away cross-section of the ingot in Figure 5 taken along lines 6-6 in Figure 5.

[0023] Figure 7 depicts division of an ingot into wafers.

#### **DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

[0024] Figure 1 illustrates schematically an exemplary decontamination system 10 that is constructed in accordance with the present invention for separating and removing technetium from nickel wafers. The exemplary system 10 includes an electro-refining cell 12 used for dissolving an anode formed of contaminated nickel. The cell 12 defines an interior anode chamber 14 for retaining an anolyte fluid 16, particularly an aqueous acid solution such as Watts nickel electrolyte. A fluid transmission conduit 18 extends from the electrorefining cell 12 to a technetium trap shown generally at 20. A fluid return passage 22 allows fluid transmission from the technetium trap 20 back to the electrorefining cell 12. A fluid pump 24 and particulate filter 26 are positioned along the fluid transmission conduit 18. The technetium trap 20 uses small amounts of nickel, from the anolyte 16, to attract the pertechnetate ions, causing the ions to plate out on a nickel cathode and thereby remove the technetium from the electrolyte. The technetium trap 20 may comprise a cementation cell that collects technetium on a second cathode (not shown). In one embodiment, the technetium trap 20 comprises an electro-refining cell containing a rod-shaped anode (not shown) that is surrounded by an annular cathode (not shown).

[0025] The anolyte 16 is returned to the anode chamber 14 of the dissolution cell 12 thereafter. Typically, small amounts of technetium (in the form of pertechnetate ions) are still present in the

anolyte 16 after leaving the technetium trap 20. For this reason, no portion of the anolyte 16 is returned to or permitted to enter the cathode chamber 36 of the dissolution cell, as this would contaminate the nickel being deposited therein.

[0026] The anode chamber 14 of the electrorefining cell 12 contains a wafer anode assembly 28 which is depicted in greater detail in Figure 4. The exemplary wafer anode assembly 28 shown includes a disc-shaped nickel wafer 30 that is supported from a stainless steel header bar 32 by a 1/4" stainless steel plate 34. A vinylester resin coats the stainless steel plate 34.

[0027] A cathodic chamber 36 is enclosed by a housing 38 within the cell 12. The cathodic chamber 36 is filled with a catholyte solution 40, and a cathode assembly 42 is submerged within the catholyte solution 40. The catholyte solution also may comprise Watts nickel electrolyte. As Figure 1A illustrates best, the catholyte solution 40 can be maintained at a higher level than the anolyte solution 16 which provides a positive pressure to help prevent entry of anolyte fluid 16 into the cathodic chamber 36. An exemplary cathode assembly 42 is shown in greater detail in Figure 3 and includes a rectangular cathode plate 44 that is suspended from copper header bar 46 by nickel electrode straps 48. The electrorefining cell may consist of more than one anode and cathode assembly. In operation, multiples of the anode and cathode assemblies may be located in a single cell. Then several cells could be connected to increase production. In this case, the anolyte pump, filter, and technetium trap could be centralized for the entire system. As can best be appreciated by the plan view of Figure 2, the anode wafer 30 is spaced about 5 inches from the cathode plate 44 during use. For clarity, the cathode plate 44 is shown apart from the cathode housing 38. The cathode plate 44 is wider than the anode wafer 30, and the anode wafer 30 is positioned centrally

with respect to the cathode plate 44 so that an approximate 45 degree angle of departure is established.

[0028] The cathode housing 38 includes a cationic membrane 50 (partially depicted in Figure 1) that completely surrounds the cathode assembly 42. The cationic membrane 50 is an ion selective membrane that permits passage of nickel ions but blocks passage of pertechnetate ions. Thus, the membrane 50 allows nickel ions to plate out on the cathode plate 44 while preventing technetium from entering the cathodic chamber 36 and plating out on the cathode plate 44. An electrical power source 52 is interconnected with both the anode assembly 28 and the cathode assembly 42 and provides an electrical potential of between 3 to 4 volts between the two.

[0029] In operation, the power source 52 energizes the anode assembly 28 and cathode assembly 42 to dissolve the anode wafer 30 within the anolyte solution 16 thereby placing nickel ions and pertechnetate ions into solution. The electro-refining cell 12 will have an electrical potential of 3 to 4 volts (preferred embodiment of 3.6V) applied to the anode assembly 28 and cathode assembly 42 at 20 to 25A/ft<sup>2</sup> current density. Nickel ions pass through the cationic membrane 50 and are plated onto the cathode plate 44. The pump 24 flows the anolyte solution 16 through the fluid transmission conduit 18 toward the technetium trap 20. The fluid movement caused by the pump 24 also acts to agitate the chemicals. En route to the technetium trap 20, the particulate filter 25 removes particulate matter from the fluid 16. The technetium trap 20 removes pertechnetate ions from the anolyte solution 16 and, after removal, the fluid 16 is returned via the fluid return passage 22 to the anolyte chamber 14 of the electro-refining cell 12. As the fluid 16 entering the anolyte chamber 14 through the return passage 22 has been substantially divested of pertechnetate ions, nickel ions in this returning solution are available to plate onto the cathode plate 40.



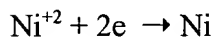
[0030] The geometry of the wafer anode 30 and the cathode plate 44 are particularly advantageous in this plating process. The wafer anode 30 is circular, or disc-shaped, and it is also physically smaller than the cathode plate 44. Figure 2 illustrates that the throwing angle for the wafer anode 30 is approximately 45 degrees. The proximity of the anode wafer 30 and the cathode plate 44, and the reduced size and shape of the anode wafer 30, compensates for the effect of the throwing angle and, therefore, provides a smoother surface of deposited nickel upon the cathode plate 44.

[0031] Referring now to Figures 5 and 6, an exemplary nickel ingot 60 is illustrated. The ingot 60 is substantially cylindrical and, as the cross-sectional views illustrate, has three internal morphological regions that have resulted from the manner in which the cylindrical ingot 60 naturally cooled following its formation. Ingots, such as ingot 60, are formed by molding molten nickel into a substantially cylindrical mold and allowing the molten nickel to cool into its substantially cylindrical shape. There is a radial outer region 62, an intermediate region 64 and a central region 66. The outer region 62 is the chilled zone where metal forming the ingot 60 quickly froze against the mold wall. After the outer region 62 was formed, columnar grains grew within the intermediate region 64 perpendicular to and inwardly from the liquid solid interface. The intermediate region 64 therefore contains interlocking crystalline structures. As the solidification process proceeds, the last metal to solidify is in the central region 66 of the ingot 60. In this central region 66, the metal is equiaxed.

[0032] Figure 7 illustrates the manner of creating wafer anodes from a cylindrical ingot 60. Thin wafers 68, 70, 72, 74 are saw cut from an axial end of the ingot. A preferred thickness for the wafers is approximately 2.5 inches although other suitable thicknesses may be used.

The use of disc-shaped wafers of substantially pure nickel as anodes, when compared to use of rectangular nickel sulfide matte anodes has proven quite advantageous as well as effective in decontamination. First, the intertwined crystalline structure of the intermediate region 64 lends structural strength to the anode during the dissolution process. As a result, the anode is less likely to fail mechanically during the electro-refining process. Matte anodes cast from nickel metal lack this intertwined crystalline structure and, therefore, are more likely to fail. Additionally, the obtaining of wafers directly from substantially pure nickel ingots saves time, effort and money as compared to the creation of matte anodes since the steps of melting and casting are eliminated. The wafer is easily affixed to the stainless steel header plate 34 and supporting header bar 32 by welding.

[0033] Circulation of fluid through the cathodic chamber 36 and filtration results in even plating of technetium onto the cathode plate 44 and the removal of contaminants from the fluid 16. Other contaminants, such as uranium, will not deposit onto the cathode plate 44. An amount of plating may be predicted using the following equations:



$$E = 58.70/2 = 29.35\text{g/equal weight}$$

$$I = (20 \text{ amps/ft}^2/\text{side} \times 3' \times 3' \times (2 \text{ sides/cathode})) = 360 \text{ amps}$$

$$W = \frac{(29.35\text{g/sq. wt.}) (360 \text{ amps}) (1 \text{ hr.}) (3600 \text{ sec./hr.})}{\text{Faraday } 96,500 \text{ amp sec/eq. wt.}} = 394.1 \text{ grams at } 100\% \text{ C.F.}$$

Assume 90% C.F. = 354 g or approx. 18.71 lbs. Ni per cathode in 24 hours

Faraday = 96,500 coulombs

W = Wt in grams

t = Time in seconds

E = Equivalent atomic weight I = Current in amps

It is noted that in actual testing of the inventive process, current efficiencies of 80% to 90% have been achieved.

[0034] While the invention has been shown in only some of its forms, it should be apparent to those skilled in the art that it is not so limited, but is susceptible to various changes without departing from the scope of the invention.

FIG. 2 is a schematic diagram of the invention.